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CONTACTS BETWEEN CHALCOGENIDE GLASSES, METALS AND SEMICONDUCTORS

H. K. Henisch

Pennsylvania State University

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Materials Research Laboratory
The Pennsylvania State University
University Park, Pennsylvania 16802

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Contacts Between Chalcogenide Glasses, Metals and Semiconductors

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1. Introductory Note

This is the final report relating to contract work carried out between June 1, 1970 and May 31, 1973. Its delay was due to the belief that the report could be deferred while a renewal proposal is pending.

The main purposes of the research were the elucidation of switching mechanisms and the exploration of systems with contact materials which can be electronically altered in situ.

2. Review of Results and Current Status*

All the work done under this contract was concerned with threshold switching in multicomponent chalcogenide glass alloys. The initial emphasis was on "Grand Principles" and, in particular, on the respective roles played by thermal and non-thermal processes. A decision on this point was considered essential, to permit a realistic evaluation of the subject as a whole, not only in academic terms but as regards its commercial future. There was also a need to develop new measurement procedures, designed to reveal characteristics of switch behavior other than the voltage-current relationship. These have been referred to as "secondary switching characteristics". In the circumstances, it was important to restrict the number of variable parameters; accordingly, nearly all the measurements were performed on $Te_{40}As_{35}Ge_{7}Si_{18}$ layers, or else on compositions closely similar. This is a typical material for the preparation of threshold switches. The systematic variation of switch material was not part of the initial program, though some measurements on memory type material and some on a non-chalcogenide glass ($CdAs_2Ge$) were done during the closing stages. For a given type of alloy, it is well known that switching behavior is not sensitively dependent on small compositional changes; the significance of the understanding already gained is therefore believed to be much wider than a single starting com-

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*Results obtained here, unless otherwise stated.

position would otherwise suggest. Most of the specimens used were placed at the disposal of the principal investigator by Energy Conversion Devices, Inc.; some were deposited here by flash evaporation or else by RF sputtering from an ECD cathode.

At the outset of this research, most outside observers and perhaps also most activists in the field were inclined to regard threshold switching as a purely thermal process. The corresponding models relied on the heat balance equation in its simplest form:

$$\nabla \cdot (K \nabla T) + j^2/\sigma = 0 \qquad (1)$$

subject to suitable boundary conditions. [K = thermal conductivity, T = temperature, j = current density, σ = electrical conductivity.] The only key assumption concerned the temperature dependence of σ, usually taken to be

$$\sigma = \sigma_0 \exp(-\Delta E/kT) \qquad (2)$$

Although such models were able to account for a sudden resistance collapse at a definite threshold voltage V_{TH}, they did not survive for long, because they failed to reproduce the observed linearity of the relationship between V_{TH} and film thickness. They also failed to provide a convincing picture of the high conductance ON-state as a separate part of the V-I characteristic, nor for the discontinuous nature of the return to the OFF-state. It has recently been shown by Adler and co-workers that, when correctly analyzed, such models do not lead to non-stabilizable ("ovonic") switching at all.

Modifications were therefore introduced at an early stage. They took the form of a field dependent conductivity $\sigma(F)$. Some of the corresponding models could be solved explicitly after the introduction of simplifying approximations, others had to be solved by computer. In each case, the introduction of $\sigma(F)$ led to a much better fit and, indeed, to superficially fair agreement with the primary switching characteristics. Even at that stage, such models should not have been called "thermal", since the electrical terms played an es-

sential role. "Electrothermal" would have been a better nomenclature, but, in the heat of the debate surrounding the whole field, this important distinction was rarely made. Moreover, the quality of the agreement with the primary switching characteristics distracted attention from the lack of agreement with almost every secondary switching characteristic (pulse response, recovery processes, temperature dependence, etc.). Of course, it also took time for the secondary characteristics to become better known.

Thermal models were always based on the notions (a) that power is dissipated, and (b) that the corresponding temperature rise (in a highly temperature sensitive material) is bound to have electrical consequences. Of course, there was never any chance that the temperature rise might be miraculously avoided; but this does not by itself prove the thermal nature of switching. After all, the same arguments apply to a transistor. We do not consider a transistor "thermal", because the essential transistor action remains when the power dissipation is extrapolated to zero. It was clear at the outset that an ovonic threshold switch would have to be tested, in corresponding terms, on the basis of the same criterion. That was one of the initial tasks; not a simple one because the consequences of heating and the consequences of electronic disequilibrium are superficially alike: both cause the systems resistance to diminish. As long as one is limited (effectively) to resistance measurements on a two-terminal system, the distinction between the two types of effects was not expected to be a straight-forward matter.

A "rare double pulse" technique was devised to solve this problem (Fig. 1a). "Rare" refers to the low repetition rate of a pulse pair, the objective being to keep the average power dissipation low. The second pulse of every pulse pair is used as a diagnostic tool for investigating the consequences of the first, and its own power dissipation is kept at a minimum. The basic fact that a recovery process is associated with switching events (Fig. 1d) has been known for a long time. If switching were primarily thermal, then the recovery could be simply

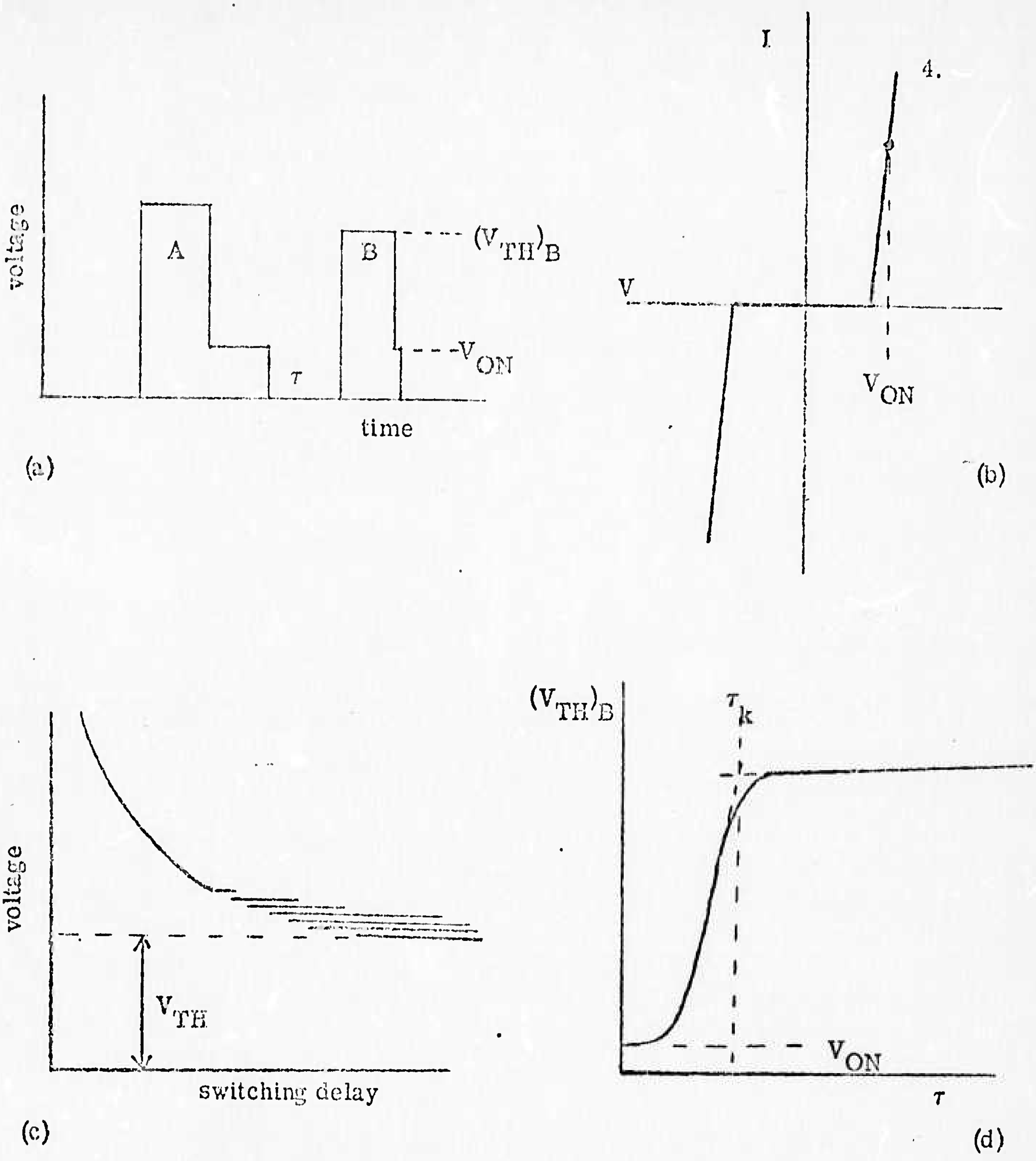

Fig. 1 (a) "Rare double pulse" method.

(b) The transient ON-characteristic (TONC).

(c) Dependence of switching delay on overvoltage; statistical character of threshold switching.

(d) Short-term memory of threshold switches.

ascribed to cooling, i.e. to the heat loss after the initial switching pulse. However, by means of the double pulse technique, it was demonstrated that switching of the second pulse, though influenced by the existence of the first, was totally independent of its power and total energy. The experiments show that the recovery is non-thermal, and this strongly suggests that switching is essentially non-thermal also, even though some heating must always be present. Experiments carried out to reveal the nature of the ON-state (by a modification of the rare double pulse technique), and the nature of the observed switching delay, reinforced that particular conclusion. By now, the electronic component of threshold switching is widely accepted, even though individual workers in the field continue to have personal preferences as regards the choice of models. The remaining question was whether the electronic component, recognized as essential, might actually be sufficient to cause switching even if the thermal component could be suppressed. The change of outlook was profound; what a few years earlier had been regarded by many as a purely thermal artefact, became a candidate for consideration as a new form of solid state electronics.

The notion that one is dealing with an electronic phenomenon has been strongly reinforced by van Roosbroeck and his co-workers. In a series of distinguished papers, they have pointed out that semi-insulators cannot be simply regarded as "poor" semiconductors. New phenomena are expected to occur as a result of the fact that, in most of these materials, the dielectric relaxation time (τ_d) exceeds the carrier lifetime ($\tau_?$). The suggestion is that this relationship has far-reaching consequences, including some which, according to the authors, can lead to switching. To be sure, the van Roosbroeck model has been under criticism in the literature (e.g. for neglecting diffusion processes), and its final predictions may be different from those made to date. Nevertheless, the "relaxation" aspects of the subject are now recognized as deserving close attention. In many laboratories, all over the world, they are now receiving it.

Demonstrations of the fact that threshold switching is not essentially thermal had to be followed with investigations designed to reveal what threshold switching is. In this connection, extensive series of experiments on the ON-state were pursued. They concerned themselves in the first instance with the manner in which the ON-state (Fig. 1b) responds to transient displacements. The results suggested

(a) that the ON-state consists of a dense electron-hole plasma,

(b) that the total ON-state conductance is barrier controlled (a conclusion which had been reached by previous workers on quite different grounds),

(c) that the barriers are made up of free carrier space charges (which accounts for temperature insensitivity), and

(d) that they are tunnelled through unless distorted in the direction of increased barrier thickness.

In due course, the effective lifetime of the plasma ($\approx 10^{-7}$ secs) was also determined by pulse measurements and its sensitivity to contact conditions established. There is now some doubt as to whether the measurements yielded a true bulk recombination time, since the possibility of carrier loss to the electrodes cannot be excluded. Calculations were also made on Fowler-Nordheim emission through a free-carrier space charge, giving good agreement between calculated and observed ON-state characteristics. As a result, it may well be that the ON-state is now better understood than other parts of the V-I switching characteristic.

The OFF-state is characterized by a voltage-dependent conductance, and though some rectification is observed, it was quickly established that the voltage dependence is mostly a bulk property. The idea of a field dependent conductivity is therefore justified, even though a satisfactory explanation remains be found for it. A number of different explanations have been proposed, e.g.

(a) the Poole-Frenkel Effect,

(b) impact ionization,

(c) field-assisted hopping, and

(d) heterojunction effects (F. E. Williams).

The Poole-Frenkel effect appears to yield the best fit, but the underlying arguments are not wholly convincing. In particular, it is not clear how the Poole-Frenkel arguments can apply to carriers in traps (rather than in donors or acceptors). In this connection, the graded band gap models developed by F. E. Williams and co-workers are of great interest because of their conceptual novelty and because they suggest a plausible mechanism for the field-dependent conductivity, and one which is in principle applicable over a wide temperature range. On the other hand, recent experiments on threshold material performed (albeit in a different context) here have shown that the photoconductivity $\Delta\sigma_L/\sigma$ is virtually independent of field up to threshold fields, and this strongly suggests that we are dealing with a mobility effect, i.e. with option (c) above.

Whatever the final decisions may turn out to be on this point, there are now reasons for believing, contrary to earlier opinions, that the non-linearity of the OFF-state is an incidental phenomenon and is not intimately connected with the character of the threshold condition. In part, this conviction comes from the (local) observation that threshold switching in organic polymers is associated with linear pre-threshold characteristics.

The work under this contract was also concerned with contact properties and, in particular, with the behavior of contacts between single-crystal and amorphous semiconductors. This line of experimentation demonstrated that there is electronic interaction between contacting and contacted material, leading to unusual V-I characteristics and unusual photo-effects, different for n-type and p-type semiconductors. The matter is important, partly because no such effects can be expected on the basis of any thermal switching model, and partly because all (inert) metallic contact materials (and graphite) had been found to exhibit identical behavior. A beginning has been made to clarify the situation, but much remains to be done. The great advantage of semiconductor electrodes is, of

course, that their carrier concentration can be altered in situ, e.g. by illumination, as shown in Fig. 2.

In systems so new, care must be taken to distinguish between intrinsic properties (i.e., modes of behavior directly involved with the switching process) and incidental artefacts, instabilities or deterioration during use. For this reason (inter alia) experiments were undertaken on "mode-of-address" effects. They revealed variations of switch behavior depending on the rate of voltage increase towards the threshold point. These effects, arising from an internal polarization, are regarded as incidental rather than fundamental, but they do point to the need for standardized measurement procedures. Experiments performed under AC and pulse conditions do not yield comparable results. Similarly, experiments are not comparable unless performed at the same overvoltage and under identical regimes of average power dissipation. Enormous pitfalls await the unwary, especially in connection with AC measurements at variable frequency. Moreover, as overvoltages and current levels are increased, it is quite inevitable that thermal factors should intervene at some stage, as they do in all other electronic devices. Investigations of the intrinsic mechanism must therefore confine themselves to minimum operating voltages and power conditions. Appropriate procedures had to be devised in the course of the research, just as the technique of transistor measurements had to be worked out during the years after 1948.

Having acknowledged that power dissipation is bound to play some part, an attempt was made to identify and measure that part. Assessments of filamentary temperature rise have been made. Because they are indirect, great precision cannot be expected from such attempts. "A few degrees" (e.g., 8-12°C) are the best available estimates, depending on the ON-current, of course. [It is interesting to note that the estimates much more confidently quoted in the literature vary from 20°C to several hundred °C, equally good agreement being claimed for all such values.]

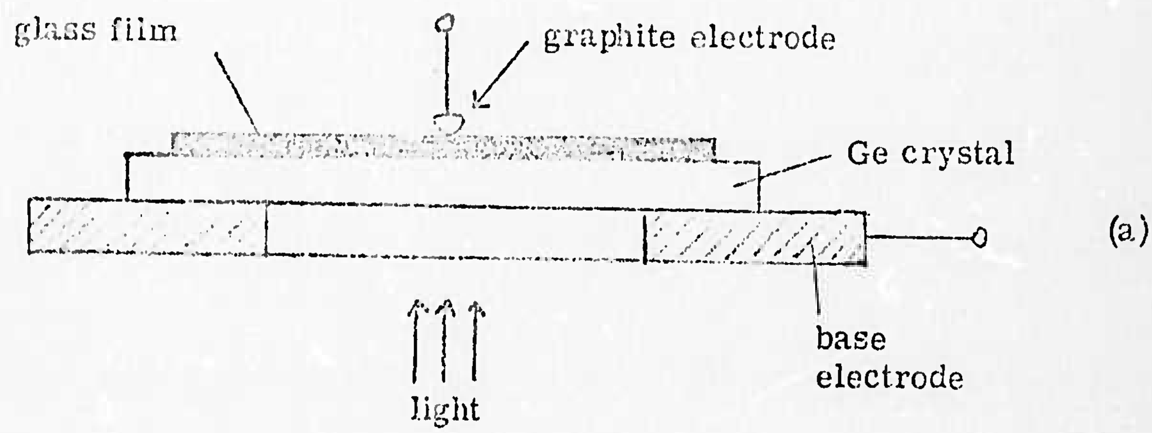

Fig. 2 Switching film with asymmetrical electrode structure, one electrode being crystalline germanium.

The "minimum power" clause can be readily illustrated by reference to measurements of the switching delay, one of the characteristic features of any threshold switching system (Fig. 1c). It was shown that the time distributions are much wider than is generally believed, e.g. between 3 μsec and 30 μsec, when the applied voltage is very close to threshold. During the delay, the current has been shown to be absolutely constant, which makes thermal effects highly implausible. With increasing overvoltage, the distribution narrows very rapidly. At the same time, the threshold current during the delay ceases to be constant, but rises in a manner highly suggestive of heating. Any mechanism proposed to account for switching must be capable of reflecting the statistical character of the switching delay at zero overvoltage, as well as the constancy of the threshold current. Clearly, the switching delay is not a waiting period for something to heat up, it is a waiting period for a random ("nucleating") event. A tentative explanation has been suggested in terms of impact ionization by analogy with the dielectric breakdown in gases.

The nature of the instability point is, of course, one of the principal issues. It is known from the work of van Roosbroeck, Keilson, Casey and Queisser that $\tau_d = \tau_\ell$ marks the condition under which an initially neutral electron-hole cluster would separate into positive and negative space charges respectively. Accordingly, the condition $\tau_d = \tau_\ell$ was taken as the threshold criterion in a model formulated by S. H. Lee and the Principal Investigator. The hypothesis was in numerical agreement with many observations, and accounted for (a) the relationship between applied voltage and switching delay, (b) the temperature dependence of the threshold voltage, (c) Haberland's results whereby every switching event demands the passage of a minimum charge, and (d) the temperature-independence of the threshold current at low temperatures. Nevertheless, it had to be abandoned, at any rate, pending further clarification. If $\tau_d = \tau_\ell$ were to constitute the threshold criterion, then the pre-threshold conductance should be characterized by $\tau_d > \tau_\ell$ and should therefore exhibit typical "relaxation semiconductor" behavior. We have no evidence that it does so in the cases here examined.

In more general terms, consideration has also been given to the relationship between switching and band structure. The Cohen-Fritzsche-Ovshinsky (CFO) model for the band structure of multicomponent chalcogenide alloys was not originally proposed as an explanation of switching, but has been found peculiarly helpful in this context. The same applies to all other band models which envisage full and automatic compensation. It is in a fully compensated material that current-limiting bulk space charges can most easily be avoided. This has been demonstrated by the fact that highly compensated crystalline layers also exhibit switching, e.g. thin layers of silicon. In a crystal, complete compensation is always difficult, and obtainable only as the outcome of skillful doping; in a multi-component glass, it is believed to be automatic, and this is thought to be the intrinsic reason for the suitability of these materials for threshold switching. Certainly, perfect charge compensation is demanded for all models which associate the ON-state with the existence of a high density electron-hole plasma. The fact that this association is realistic has since been demonstrated by Kolomiets and co-workers in Leningrad. They observed radiative recombination from their switches when in the ON-state.

No doubt our picture will undergo various stages of refinement during the next few years, but whereas many aspects remain to be clarified (a proposal for the continuation of this research is pending) threshold switching is no longer the impenetrable mystery it seemed to be a few years ago, nor can it be dismissed as "a type of thermistor effect". On the contrary, it remains a topic of great interest in "pure" and "applied" contexts, and is thought to deserve much more attention and support than it is now receiving. A list of publications resulting from work on the present contract is given below.

3. Publications

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Burgess, W. D. and Henisch, H. K., "Pre-threshold Conductance and Polarization Effects in Amorphous Semiconductor Switches", Solid State Electronics 16, 15 (1973).

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Lee, S. H. and Henisch, H. K., "Thermal and Non-thermal Processes in Threshold Switching", J. Non-cryst. Solids 9, 108 (1972).

Lee, S. H. and Henisch, H. K., "Threshold Switching in Chalcogenide Glass Films", Appl. Phys. Letters 22, 230 (1973).

Lee, S. H., "The ON-state in Threshold Switches", Appl. Phys. Letters 21, 544 (1972).

Smith, W. and Henisch, H. K., "Threshold Switching in the Presence of Photo-excited Carriers", phys. stat. sol. (a) 17, K 81 (1973).

4. Note on Personnel

For various periods, the collaborators mentioned below were engaged in this work, in addition to the Principal Investigator.

Dr. S. Lee (Research Associate)

Mr. D. Burgess (Graduate Assistant)

Mr. R. Pryor (Graduate Assistant)

Mr. G. J. Vendura, Jr. (Graduate Assistant)

Mr. W. R. Smith